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Polymerization Kinetics and Nanostructure Evolution of Reactive Lyotropic Liquid Crystals with Different Reactive Group Position

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ABSTRACT: The synthesis of polymers with inherent nanostructure has recently received much attention because of the wide range of potential application in which these materials could be used. To understand the factors that affect the nanoscopic order preservation upon polymerization, this work examines the influence of reactive group position in polymerizable surfactants that form reactive lyotropic liquid crystals (LLCs) on polymerization kinetics and order before and after polymerization. Less ordered LLC phases are formed with reactive surfactants bearing reactive groups in the nonpolar tail compared to reactive surfactants with reactive groups near the polar head. The polymerization kinetics are influenced by both the LLC order and the position of the reactive group. Higher polymerization rates are observed for reactive surfactants with the reactive group near the polar head with increasing surfactant concentration and LLC order. On the other hand, lower polymerization rates are observed for the reactive surfactant with the reactive group in the aliphatic tail at higher surfactant concentrations and LLC order. This behavior is mainly due to segregation of the reactive groups in different regions of the LLC phases as indicated by an apparent increase in both the propagation and termination kinetic constants. When using initiators that induce higher polymerization rates, greater LLC order preservation is observed after polymerization. Also, by using higher light intensities, the resulting polymer exhibits higher degrees of LLC order retention than that observed when polymerization is initiated with lower light intensities and corresponding lower polymerization rate.

Introduction

The controllable synthesis of nanostructured materials has recently received much attention due to interesting properties such as high surface area to volume ratios, enhanced mechanical properties, and nanoscopic order. These properties make such materials useful for applications such as separations, catalysis and in emerging areas including DNA delivery and tissue engineering.[1−4] A number of systems have been developed in which nanoscale order is exhibited including block copolymers and zeolites.[5,6] In many of these materials the formation of the nanostructure is driven by self-organization of molecules into ordered arrays with nanoscopic dimensions. One particularly versatile method offering great promise in the controllable synthesis of nanostructured polymeric materials involves self-assembly of amphiphillic molecules into highly ordered lyotropic liquid crystalline (LLC) arrays.[7]

Lyotropic liquid crystals (LLCs) are surfactant based systems which organize into different ordered structures depending on concentration, temperature, and the packing preference of the surfactant molecule.[8,9] LLC phases exhibit positional and orientational order as seen in solids while still having the rheological properties of liquids. At low surfactant concentrations sphere-like micelles are formed at the critical micelle concentration. With higher concentrations of surfactant molecules in water, a variety of LLC phases can form including hexagonal, lamellar, and cubic geometries.[9] The inverse of these phases can also be observed in some systems.[8] Unfortunately, LLC systems lack mechanical stability and therefore cannot be used for nanostructured material applications. The fact that LLC phases exhibit nanometer size features makes these systems ideal candidates to be used as templates for the creation of nanostructured materials. By changing the concentration of the amphiphilic molecule, access to different templates is achieved, enabling the creation of polymers that exhibit LLC nanostructures.

The use of LLCs as templates for the creation of nanostructured materials has been widely explored.[10−12] The reaction employed to create organic nanostructure materials based on LLCs has proven to be very important. In many systems using different reaction mechanisms, retention of structure during polymerization is not achieved due to phase separation of the polymer from the template.[13] Photopolymerization seems to be the best method to perform these reactions due to its inherent speed, thereby allowing the polymer network to lock-in the structure of the template on a faster time scale than phase separation or reorganization of the template can occur.[14,15] For example, greater order retention after polymerization is observed for light induced polymerizations compared to thermally induced polymerizations.[14,15] Much research in LLC polymer templating has focused on reducing phase separation through greater understanding of the role of LLC stability, monomer chemistry, polymerization behavior, and environmental factors on the retention of template structure within the formed polymer network.[12−17]

The polymerization kinetics in LLCs exhibit a strong dependence on the order before polymerization and also play a major role in the polymer structure retention, with enhanced structure retention observed in LLC phases where higher polymerization rates are observed.[13−15] Other polymerization conditions such as temperature, initiator type, and surfactant type have an effect on the polymerization kinetics and, therefore, on the polymer structural evolution.[18−20] For example, the polymerization of acrylamide monomers in various Brij surfactants (block copolymer)

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exhibit a 10-fold increase in polymerization rate in LLC phases compared to polymerization in isotropic systems.[15] This behavior is induced by segregation effects which produce higher local monomer concentration and diffusional limitations in ordered phases.[15]

The polymerization kinetics in LLC systems are highly dependent on the phase in which they are polymerized and also on spatial segregation within the LLC.[15,18−20] Oil- and water-soluble monomers exhibit opposite kinetic trends because they localize in distinct and different domains of LLC phase structure.[15,18−20] Both the localized double bond concentration and diffusional limitations change depending on the LLC phase causing significant changes in rate behavior. Such changes are a reflection of the segregation of monomer within the liquid crystalline phase and thus can provide indications of how polymer nanostructure develops in the ordered media. Oil- and water-soluble monomers could create polymers with much different structures due to their mode of segregation, even within the same LLC template phase. Other studies have shown that initiator segregation plays an important role in directing the photopolymerization kinetics in LLC media.[20] Initiators forming large radical fragments exhibit higher efficiency in a lamellar phase relative to the cubic phase. Typically, higher relative efficiencies of hydrophobic initiators are observed in phases with greater surfactant concentrations and low water content. Relatively hydrophilic initiators show the opposite dependence on surfactant concentration.

Another means of creating polymer with LLC nanostructure utilizes reactive surfactants that form LLCs. Reactive LLCs have the advantage that the monomer itself forms the LLC structures which could potentially decrease the phase separation typically observed in templated LLC systems. Several applications for polymers made from reactive LLCs have been explored including nanofiltration, water desalination, catalysis, and chemical protection.[21−26] As with templated LLC systems, the polymerization kinetics in reactive LLCs are dependent on the LLC phase in which the polymerization occurs.[13] Recent studies in reactive LLCs formed by monomethacrylate quaternary ammonium surfactant monomers in water demonstrate that more ordered lamellar phases, in which higher polymerization rates are exhibited, are retained after polymerization while hexagonal phases that polymerize at slower rates are not retained.[13] The high speed of reaction associated with the lamellar phase seems to enable the entrapment of the LLC structure after polymerization while the slower reaction associated with the hexagonal phases allows the nanostructure to rearrange into a more thermodynamically stable structural conformation. Also, increasing the nonpolar tail length of the reactive surfactant phase decreases the LLC order and a decrease in the polymerization rate is observed. More recently, the importance of cross-linking has been demonstrated in preserving the LLC structure during polymerization.[27] Previous research in vesicles and other amphiphilic systems has also shown that the position of the polymerizable group, the aliphatic tail length, and temperature all have an effect in the structural evolution.[28−30]

Although much research has been done in understanding the polymerization kinetics of amphiphilic systems, further understanding of the factors affecting the kinetics and structure evolution during polymerization for templated and reactive LLC systems is necessary to allow control over the polymer structure formation. The goal of this work is to investigate the influence that the position of the reactive group in reactive surfactant monomers has on the order of the LLC phase, polymerization behavior, and structure retention. Differences in order and polymerization dynamics could be obtained simply by changing the position of the reactive group in the LLC that could, in turn, affect how the polymer structure evolves during polymerization. The phase behavior and polymerization kinetics when using surfactant monomers with reactive groups near the polar head will be compared to surfactant monomers with reactive groups in the polar tail. The polymerization rate will be studied and related to the aggregation of the different LLC phases. The influence of the type of surfactant monomer on the polymerization behavior will be evaluated by comparing rate parameters of propagation and termination within the same LLC phases. Also, the influence of initiator efficiency and light intensity on polymerization kinetics will be studied and correlated to LLC order in the resulting polymer.

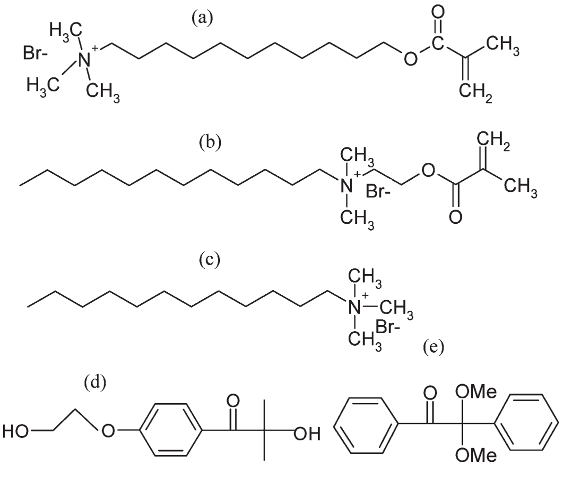

Figure 1. Chemical structures of the surfactant monomers,nonreactive surfactant and photoinitiators used in this study. Shown are (a) PM1 (reactive group in the aliphatic tail), (b) C12MA (reactive group near the polar head), (c) DTAB (non reactive surfactant), (d) 4-(2-hydroxyethoxy) phenyl-(2-hydroxy-2-propyl) ketone (Irgacure 2959), and (e) 2-Dimethoxy-1,2-diphenylethan-1-one (Irgacure-651).

Experimental Section

Materials. The quaternary ammonium surfactant monomer C12MA, with the reactive methacrylate group near the polar head, was prepared by reacting dimethylaminoethyl methacrylate (Aldrich) with dodecadecyl bromide (Aldrich) according to a method previously described.[31] The quaternary ammonium surfactant monomer PM1, which has the reactive group in the nonpolar tail, was synthesized as described elsewhere.[32] The reagents and solvents 11-bromo-1-undecanol (Aldrich), methacryloyl chloride (Aldrich), anhydrous pyridine (Aldrich), tetrahydrofuran (THF, Aldrich), and 4-methoxyphenol (Fluka) were used as received. Dodecyltrimethylammonium bromide (DTAB, Aldrich) was used as a nonpolymerizable surfactant analogue to modulate the phase behavior. The LLC systems presented in this research were prepared by mixing and centrifugating the reactive surfactant, nonpolymerizable surfactant, deionized water, and photoinitiator (Irgacure 2959, Ciba; Irgacure 651, Ciba) until a homogeneous mixture was obtained. All concentrations of surfactant, water and initiator are based on weight percentages. The chemical structures of C12MA, PM1, and DTAB are shown in Figure1.

Procedure. Polymerization rate profiles were generated by following the polymerization in real time with a Perkin-Elmer differential scanning calorimeter. A medium-pressure UV arc lamp (Ace Glass) with a 365 nm wavelength filter was used to initiate polymerization. The light intensity used was 1.5 mW/cm^2 unless otherwise indicated. Water evaporation was minimized by covering the approximately 3.5 mg samples with thin transparent films of FEP (DuPont fluorinated copolymer). Samples were purged with nitrogen for 8 min prior to polymerization to prevent oxygen inhibition. The samples were also heated to 80 °C and cooled to 30 at 10 °C/min to ensure uniform thermal contact and thickness. Isothermal reaction conditions were maintained during polymerization using a refrigerated

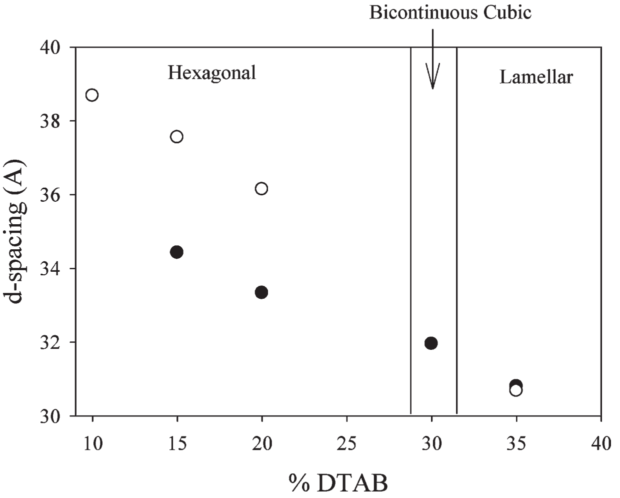

Figure 2. *d*-spacing as determined by small-angle X-ray scattering (SAXS) for the liquid crystalline phases formed for 50% C12MA (●) and 50% PM1 (○) at different DTAB concentrations in water.

circulating chiller. The polymerization rate, R_p, was determined as a function of time from the heat flow as explained in previous publications.[33] The polymerization rate of each sample was monitored at least three times. For each figure, the most representative profile was chosen. The polymerization rate as given is normalized by the initial monomer concentration, allowing direct comparison of different monomer concentrations. Maximum rates were taken from the peak in the rate profiles obtained, and double bond conversion was calculated by integrating the heat flow profiles. For these studies the theoretical value of 13.1 kcal/mol (54.8 kJ/mol) was used as the heat evolved per methacrylate double bond reacted.[34]

Apparent rate parameters for k_t and k_p were measured through a series of after-effect experiments. The steady-state polymerization rate was utilized to determine the lumped kinetic constant, $k_p/k_t^{1/2}$ as a function of time. By closing the light shutter between the UV light source and the sample at various time intervals during the polymerization, the initiation step was eliminated and the exotherm decay was analyzed by eq 1 to give k_p/k_t from the slope of a plot of reciprocal exotherm rate versus time

$$\frac{1}{R_p} - \frac{1}{R_{po}} = \frac{2k_t t}{k_p[M]} \qquad (1)$$

where R_p is the polymerization rate at time t after the light shutter is closed, R_{po} is the initial rate of polymerization when the light shutter is closed, and [M] is the double bond concentration at time t. The propagation and termination rate parameters can then be decoupled. The methodology of determining individual rate constants is also described in detail elsewhere.[35]

LLC morphology for the different samples was characterized by using small-angle X-ray scattering (SAXS). By measuring ratios in *d*-spacing calculated from the reflections in the corresponding sample profiles, the LLC order can be determined.[13] These measurements were conducted utilizing a Nonius FR590 X-ray apparatus with a standard copper target Röntgen tube as the radiation source with a Cu Kα line of 1.54 Å, a collimation system of the Kratky type, and a PSD 50 M position sensitive linear detector (Hecus M. Braun, Graz). Optical textures from LLC phases were analyzed with a polarized light microscope (Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO). By comparing SAXS profiles and polarized light microscopy images before and after polymerization, the degree of LLC order present upon polymerization was determined. A BLAK-RAY ultraviolet lamp (365 nm wavelength) was used to polymerize samples for structure retention studies. A low light intensity of 1 mW/cm^2 and a high light intensity of 15 mW/cm^2 were used by varying the distance between the lamp and the sample.

Results and Discussion

Examining the polymerization behavior has proven useful in understanding the local reaction environment and elucidating nanostructure evolution in lyotropic liquid crystalline systems. For example, the polymerization of reactive lyotropic liquid crystals exhibits changes in polymerization rate profiles that have been related to changes in structure during polymerization.[27] Additionally, the polymerization behavior of monomers templated in lyotropic liquid crystals is dependent on monomer polarity due to the segregation and ordering effects.[18-20] In a similar way, it is reasonable to believe that the position of the reactive group in reactive LLCs could have an effect on the polymerization kinetics and therefore on the resulting polymer structure. As mentioned previously, the goals of this work are to determine the effect of the position of the reactive group in the reactive surfactant on the polymerization kinetics and nanostructure of reactive LLC systems and the impact of initiator and light intensity on the resulting polymer order. By using initiators that exhibit different efficiencies and by employing different light intensities, the influence of the polymerization kinetics on the LLC order preservation after polymerization can be determined.

LLC Phase Behavior. Monomethacrylate quaternary ammonium surfactant monomers, C12MA and PM1, bearing the reactive group near the polar head and at the end of the aliphatic chain, respectively, were chosen for comparison due to their similarity in molecular structure. These surfactant monomers form micellar cubic, hexagonal, and lamellar phases when mixed in water.[36] In order to obtain various LLC phases, different concentrations of surfactant monomer need to be used which could change the concentration of the double bonds present in the system. To better understand the dependence of order and type of surfactant monomer on the polymerization kinetics, it is desirable that the double bond concentration be held constant.[17] To modulate the LLC morphology of the surfactant monomers while keeping the concentration of double bonds constant, the nonpolymerizable surfactant dodecyltrimethylammonium bromide (DTAB) was added. The molecular structure of DTAB is analogous to C12MA and PM1, therefore enabling LLC phase modulation for C12MA/water and PM1/water systems. By holding the amount of C12MA or PM1 constant and replacing water with DTAB, the formation of different LLC phases can be achieved while keeping double bond concentration constant. At 50% C12MA in water a micellar cubic phase is observed. The hexagonal phase is observed when keeping the C12MA concentration constant while replacing water with 5% to 25% DTAB. Further increases in DTAB allow formation of the bicontinuous cubic and lamellar phases at 30% DTAB and 35% DTAB respectively. Similar LLC phase modulation is observed when adding DTAB to 50% PM1 in water with the exception that the hexagonal phase is extended to 30% DTAB thereby preventing the formation of the bicontinuous cubic phase as confirmed by polarized light microscopy and SAXS.

LLC phases exhibit characteristic dimensions that can be tailored by the size of the surfactant molecule, concentration and monomer segregation. Figure 2 shows the d_{100} spacings for the unpolymerized samples of 50% C12MA/DTAB/water and 50% PM1/DTAB/water systems, calculated from primary reflections in SAXS profiles. The d_{100}-spacing decreases as the concentration of the surfactant increases and the LLC phase changes from the hexagonal to the lamellar

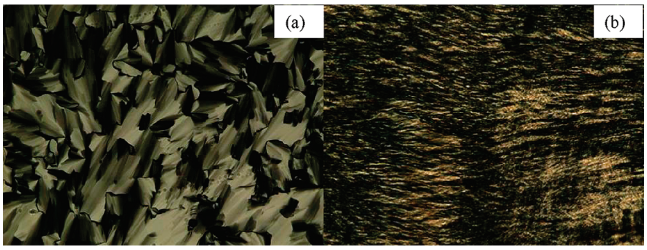

Figure 3. Polarized light micrographs for the hexagonal phases formed using (a) 50% C12MA−20% DTAB in water and (b) 50% PM1−20% DTAB in water.

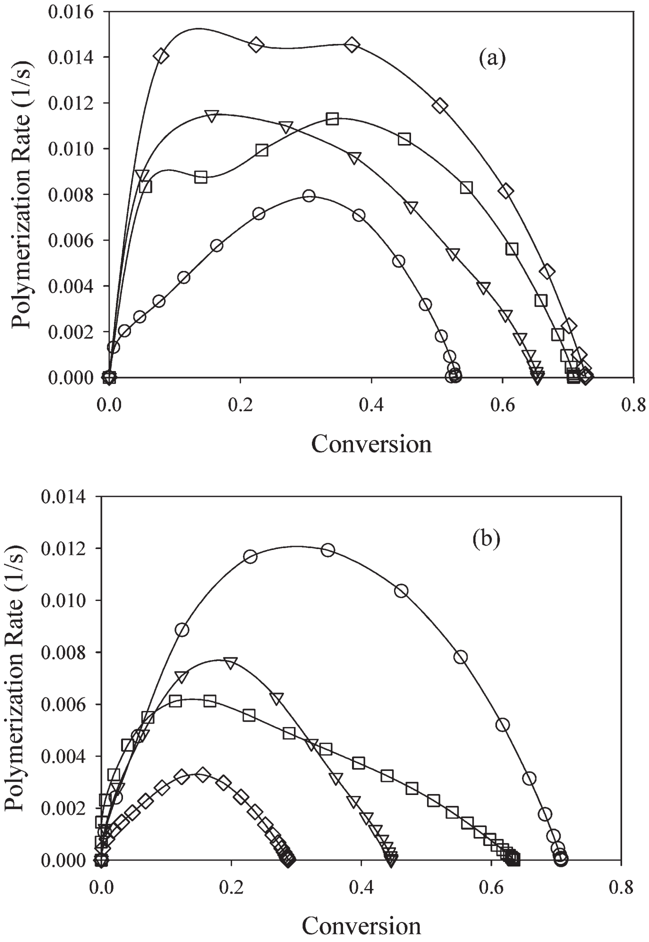

Figure 4. Polymerization rate as a function of conversion for (a) 50% C12MA-DTAB and (b) 50% PM1-DTAB at different concentrations of DTAB using I-2929 as photoinitiator. Shown in graph a are 0% DTAB-isotropic (○), 20% DTAB-hexagonal (▽), 30% DTAB-bicontinuous cubic (□), and 35% DTAB-lamellar (◇). Shown in graph b are 0% DTAB-isotropic (○), 10% DTAB-hexagonal (▽), 20% DTAB-hexagonal (□), and 35% DTAB-lamellar (◇).

phase. This behavior is due to the closer aggregation of surfactant as more molecules are present and the order increases.[13] Also, at the same DTAB concentration and LLC phase, the *d*-spacing is higher for the 50% PM1/DTAB/water system compared to 50% C12MA/DTAB/water. This behavior is directly related to the location of the reactive methacrylate group in the surfactant monomer. For C12MA, the methacrylate reactive group, which is relatively polar, is located near the polar nitrogen head. This structure allows increased LLC order and phase stability. On the other hand, the reactive methacrylate group of PM1 is at the end of the aliphatic chain, therefore polar moieties are on both ends of the molecule which may decrease the ability to form well-defined LLC phases. While LLC phases are still formed, the larger *d*-spacing indicates that the phases are not as ordered as in C12MA. Such differences in LLC order can be seen clearly in Figure 3, in which polarized light micrographs for the hexagonal phases formed using 50% C12MA/20% DTAB and 50% PM1/20% DTAB in water are shown. The polarized light micrograph for C12MA exhibits very defined focal conic textures typical of a hexagonal phase. On the other hand, the polarized light micrograph for PM1 shows a much less defined hexagonal phase.

Polymerization Kinetics. As mentioned previously, a primary goal of this work is to determine the effect of the reactive group position on the polymerization behavior within LLC phases. As such, the polymerization rate was examined as a function of LLC geometry for both C12MA and PM1 monomer systems. Samples ranging from 0 to 35% DTAB were selected as this concentration range exhibits the micellar, hexagonal, bicontinuous cubic, and lamellar phases. Interestingly, the polymerization kinetics of surfactant monomers with reactive groups in different positions exhibit very different polymerization behavior. Parts a and b of Figure 4 show the polymerization rate profiles for 50% C12MA/DTAB/water and 50% PM1/DTAB/water respectively using I-2959 as the photoinitiator. As can be seen in Figure 4a, forming the hexagonal phase by adding 20% DTAB increases the maximum polymerization rate about 40% when compared to the isotropic phase formed when no DTAB is present. Increasing the concentration of DTAB to 30% to form the bicontinuous cubic phase does not affect the maximum polymerization rate but changes in the polymerization rate profiles are observed as two peaks in the polymerization rate are present. The fastest polymerization rate is observed for the polymerization in the lamellar phase at 35% DTAB which exhibits a maximum polymerization rate about two times that observed in the isotropic micellar cubic phase. Similar behavior has been observed for the binary C12MA/water system in which the polymerization rate increases as the order increases.[13] It is important to note that two peaks are evident in the polymerization rate versus time curves for some of the LLC phases. This behavior may be attributed to autoacceleration effects associated with an increase in viscosity during the polymerization process, but recently has also been associated with changes in phase morphology for polymerization in reactive LLC phases.[13]

Interestingly, the 50% PM1/DTAB/water system exhibits completely different behavior as shown in Figure 4b. Forming the hexagonal phase by adding 10% DTAB decreases the maximum polymerization rate about 40% compared to the isotropic micellar phase formed when no DTAB is added. For the C12MA surfactant system, increasing the concentration to form a hexagonal phase results in an increase in polymerization rate. The hexagonal phase system formed with 20% DTAB exhibits a polymerization rate that is slightly lower that observed at 10% DTAB. The lowest polymerization rate is observed in the lamellar phase formed at 35% DTAB which exhibits a maximum polymerization rate that is four times lower than that observed in the cubic micellar phase. Opposite trends are also observed in the final conversion of the polymerization in the different LLC phases. Increasing conversion is observed in the C12MA systems with increasing surfactant concentration and LLC order. On the other hand, the overall double bond conversion for PM1 decreases with increasing surfactant concentration. For example, approximate conversions of 50% and 70% are obtained for the isotropic and lamellar phases respectively for C12MA, while conversions of 70% and 30% are obtained

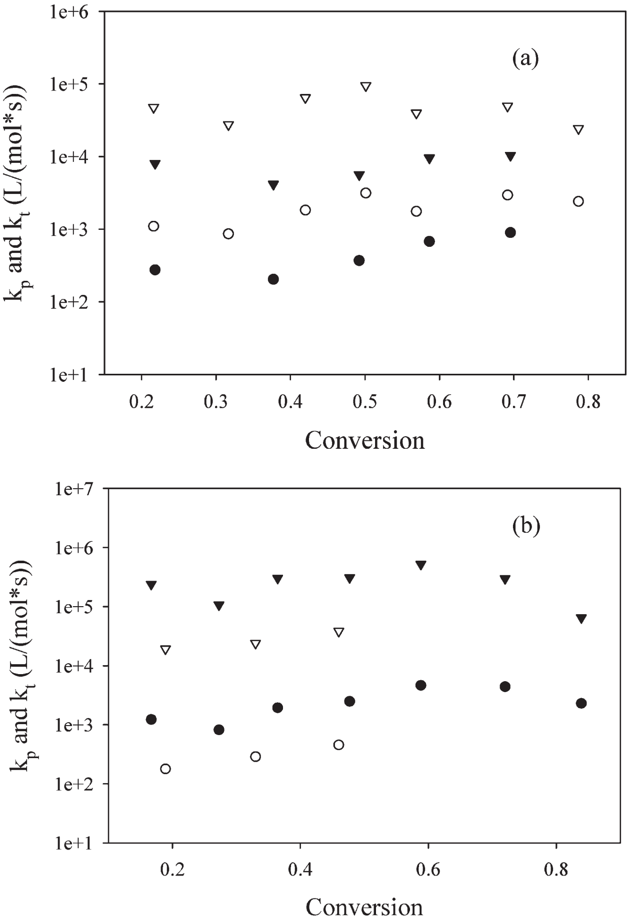

Figure 5. Termination (k_t) and propagation (k_p) rate parameters for polymerization of (a) 50% C14MA-DTAB in water and (b) 50% PM1-DTAB in water as a function of double bond conversion at 30 °C. Shown in graph a are k_p for 0% DTAB-isotropic (●), k_p for 35% DTAB-lamellar (○), k_t for 0% DTAB-isotropic (▼), and k_t for 35% DTAB-lamellar 50% (▽) in water. Shown in graph b) are k_p for 0% DTAB-isotropic (●), k_p for 35% DTAB-lamellar (○), k_t for 0% DTAB-isotropic (▼), and k_t for 35% DTAB-lamellar (▽) in water.

for the isotropic and lamellar phases respectively for PM1. This behavior could be directly related to the position of the functional groups and overall order. With increasing surfactant concentration and decreasing water concentration, the local C12MA double bond concentration will increase. This segregation affect increases the likelihood of continued propagation even when monomer mobility is limited at higher conversions. PM1 double bonds will actually decrease in local concentration with increased surfactant and nonpolar content, which appears to induce lower overall conversion.

To explain the increase in polymerization rate for C12MA and decrease in polymerization rate for PM1 when increasing the LLC order, after-effect experiments were performed to determine apparent rate parameters of propagation, k_p, and termination, k_t. These values were calculated from the steady-state polymerization rate and dark reaction exotherm decay.[35] It is important to note that the values calculated are apparent parameters as they are based on the overall reaction and do not take local concentration affects into account. Previous research has demonstrated that changes in local monomer concentration lead to significant changes in the observed or apparent values of k_p and k_t, but should not change inherent reactivity.[33] Figure 5a shows the apparent propagation and termination rate constants for the accelerated polymerization in the lamellar phase formed with 50% C12MA/35% DTAB in water and the slower polymerization in the isotropic cubic phase observed at 50% C12MA/0% DTAB in water. Over a range of conversions polymerization in the lamellar phase exhibits a k_p that is an order of magnitude higher than the value for the polymerization in the cubic micellar phase. A similar increase is also observed for the k_t values in the lamellar phase. Since the polymerization rate based on a steady state radical assumption is dependent on $k_p/k_t^{1/2}$, a similar increase of both k_p and k_t will produce an overall increase in the polymerization rate. Similar behavior has been seen for the binary C12MA/water system based on segregation effects in the LLC phases in which such increases can be directly related to double bond segregation.[13] With lower interfacial curvature the polymerizable double bonds would be more concentrated in the lamellar phase, causing a significant change in local concentration and in the polymerization dynamics.

Contrasting behavior is observed for the 50% PM1/DTAB/water system. Figure 5b shows the apparent propagation and termination rate constants for the accelerated polymerization in the micellar phase formed with 50% PM1 in water and the slower polymerization in the lamellar phase formed with 50% PM1/35% DTAB in water. In this case, the isotropic cubic micellar phase formed exhibits k_p and k_t values an order of magnitude higher than the polymerization in the lamellar phase. This behavior is the exact opposite of that observed for the C12MA system for which the k_p and k_t values are higher in the lamellar phase. The double bonds for PM1 are located at the end of the nonpolar tail, hence the reactive group will segregate in the nonpolar regions of the LLC. Therefore, higher local concentrations of double bonds are observed for the micellar phase compared to the lamellar phase that induces higher polymerization rates. These results indicate that the polymerization kinetics in reactive LLC systems is highly governed by the segregation of double bonds in the LLC phase.

The double bond segregation in LLC phases and its influence in the polymerization kinetics could affect the resulting polymer structure. Better knowledge of the segregation of reactive groups in the LLC phase could provide a better indication of its influence on order. As mentioned previously, in other systems for which monomer and double bond segregation is important, changes very similar to those observed in the C12MA and PM1 systems were reported.[33] To quantify the segregation of reactive groups in these systems a segregation factor (α) has been derived as shown in eq 2.[33]

$$\alpha = \frac{k_p}{k_p'} \qquad (2)$$

In this equation, k_p represents the values observed in the less ordered geometry, and k_p' represents the observed values for the more ordered, and hence faster polymerization. This model has been used elsewhere to understand polymerization behavior in thermotropic liquid crystals and templated LLC systems.[12,33] As shown elsewhere,[33] this value is a direct measure of the degree of segregation of the reactive groups. For the PM1/DTAB/water system k_p' is the propagation rate parameter for the faster polymerization in the isotropic discontinuous cubic phase with 50% PM1 in water, and k_p is the propagation rate parameter for the lamellar phase formed with 50% PM1 and 35% DTAB in water. In the PM1 case α is approximately 0.1 which means that the reactive groups are approximately 10 times more concentrated in the isotropic discontinuous cubic phase than in the

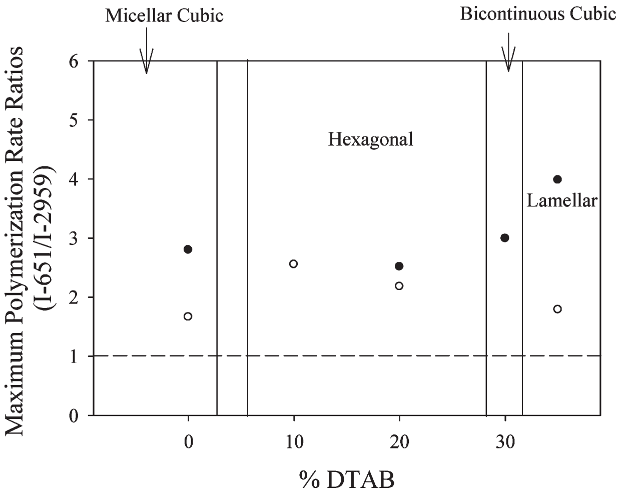

Figure 6. Maximum polymerization rate ratios between I-651 and I-2959 for C12MA (●) and PM1 (○) at different DTAB concentrations.

lamellar phase. To quantify segregation for the C12MA/DTAB/water we define k_p as the propagation rate parameter for the isotropic discontinuous cubic phase formed at a concentration of 50% C12MA in water and k_p' is the propagation rate parameter for faster polymerization in the lamellar phase. In this case α is approximately 0.07 which means that the reactive groups are 14 times more concentrated in the lamellar phase compared to the isotropic discontinuous cubic phase. Clearly, the morphology of the aggregates and the position of the reactive group in the surfactant play a major role in the segregation, local concentration of double bonds, and consequent polymerization kinetics. The fact that the reactive groups are 14 times more concentrated in the lamellar phase compared to the discontinuous cubic phase for C12MA and 10 times more concentrated in the discontinuous cubic phase compared to the lamellar phase for PM1 is directly related to the greater LLC order observed in the C12MA system. For both cases the morphology of the aggregate plays a major role in the increased concentration of double bond.

While the segregation of double bonds in the surfactant aggregates directly affects the polymerization kinetics, previous research has shown that the type of initiator also may affect the polymerization behavior, which could translate into differences in the polymer formation.[18] To gain a better understanding of the role of photoinitiation on the polymerization kinetics in reactive LLC systems, the polymerization behavior was also examined using the more efficient and less polar initiator I-651. In general, similar trends in the polymerization rate were observed for both C12MA and PM1 with I-651 when changing LLC order. The polymerization rate for 50% C12MA in water increases and the polymerization rate for 50% PM1 in water decreases as the order of the system increases. Also, it is important to mention that the polymerization rates in all the LLC phases using I-651 are much higher than when I-2959 is used as seen by the ratios of maximum polymerization rates shown in Figure 6. This behavior is due to the higher molar absortivity of I-651. For example, polymerization of C12MA in the lamellar phase using I-651 exhibits a polymerization rate that is almost 4 times that when I-2959 is used. Similarly, the polymerization of PM1 in the lamellar phase using I-651 exhibits an increase in polymerization rate that is approximately 2 times that observed when I-2959 is used. Interestingly, based only on the molar absortivity, an increase of reaction rate of approximately 3 is expected. An average maximum polymerization rate ratio of 3 is observed for C12MA among LLC phases while an average ratio of 2 is observed for PM1. Clearly other factors, such as order and initiator-monomer interactions, must drive the differences in reaction rate for the different LLC phases with different initiators. Interestingly, smoother reaction rate profiles with less pronounced double peaks are seen when using I-651 compared to I-2959. This behavior is quite obvious in the C12MA system and could indicate differences in LLC order retention after polymerization.

Kinetic Control of Polymer Nanostructure. Previous work has shown that the rate of polymerization has a direct effect on the structure evolution of polymers in LLC systems.[13,27] Faster polymerizations create polymers that may be more likely to retain the original LLC order compared to slower polymerizations. The fact that increases in polymerization rate are observed when using I-651 compared to I-2959 could have an effect on the LLC order preservation during the polymerization. To further explore the effect of polymerization kinetics on the structure evolution, small-angle X-ray scattering profiles were obtained before and after polymerization. Figure 7a shows the SAXS profiles for the hexagonal phase formed at 50% C12MA/20% DTAB in water before and after polymerization using I-2959 and polymerized with a low light intensity of 1 mW/cm^2. Before polymerization the SAXS profile shows two reflections that exhibit a ratio of $1{:}1/3^{1/2}$, indicative of a hexagonal phase. Upon polymerization the intensity of the primary peak decreases substantially and the secondary peak disappears. This behavior indicates that the LLC order is significantly disrupted during the polymerization.

Interestingly, greater retention of LLC order is observed in the more rapid polymerization of 50% C12MA/20% DTAB in water when using I-651 as the photoinitiator. Figure 7b shows the SAXS profiles for the hexagonal phase formed at 50% C12MA/20% DTAB in water before and after polymerization using I-651. Before polymerization the SAXS profile shows two reflections that exhibit a ratio of $1{:}1/3^{1/2}$, indicative of a hexagonal phase. Even though upon polymerization the primary and secondary peaks decrease slightly, suggesting some order is lost during polymerization, the LLC order is preserved to a much greater degree compared to the polymerization using I-2959. These results confirm that the polymerization kinetics have a direct effect on the structure evolution of reactive LLC systems. The higher polymerization rates observed when using I-651 enable greater retention of LLC order by locking the structure in place before molecular rearrangement occurs. In order to confirm that the reaction rate has an influence on the LLC order preservation after polymerization, polymerization was also conducted at higher light intensity. Figure 7c shows the SAXS profiles for the hexagonal phase before and after polymerization using I-651 and polymerized with a much higher light intensity of 15 mW/cm^2. The intensity of the primary peak after polymerization increases slightly while the ratio height to width at half height does not change significantly, suggesting no major change in order during polymerization.[15,27] Even though the intensity of the secondary reflection decreases, it is still evident suggesting that some degree order is retained. These results confirm that the structural evolution of reactive LLC systems is highly governed by the polymerization kinetics with greater structure retention observed at faster polymerization rates.

Higher induced polymerization rates preserve the LLC order to a greater extent after polymerization for C12MA reactive surfactant with the reactive groups near the polar head. If the reactive group is in the nonpolar tail of the

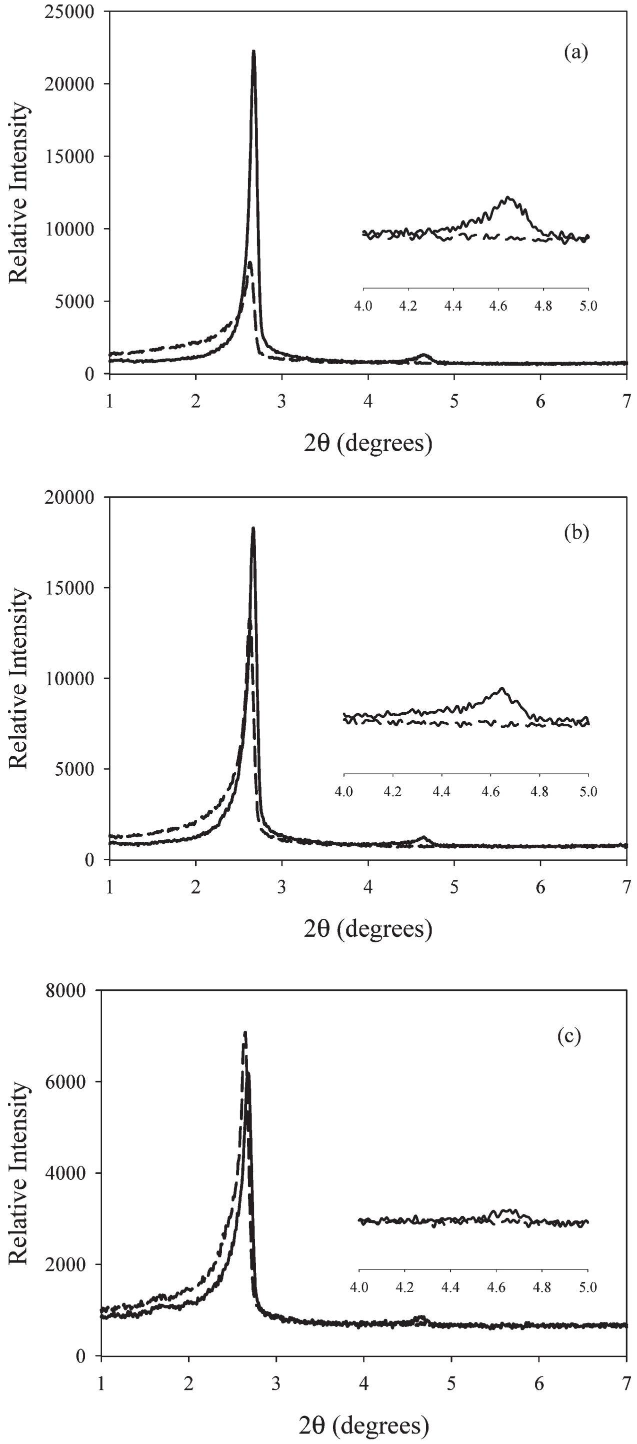

Figure 7. SAXS profiles for the hexagonal phase formed with 50% C12MA-20% DTAB in water using (a) I-2959 at 1 mW/cm^2, (b) I-651 at 1 mW/cm^2, and (c) I-651 at 15 mW/cm^2 before (—) and after (□ □) polymerization.

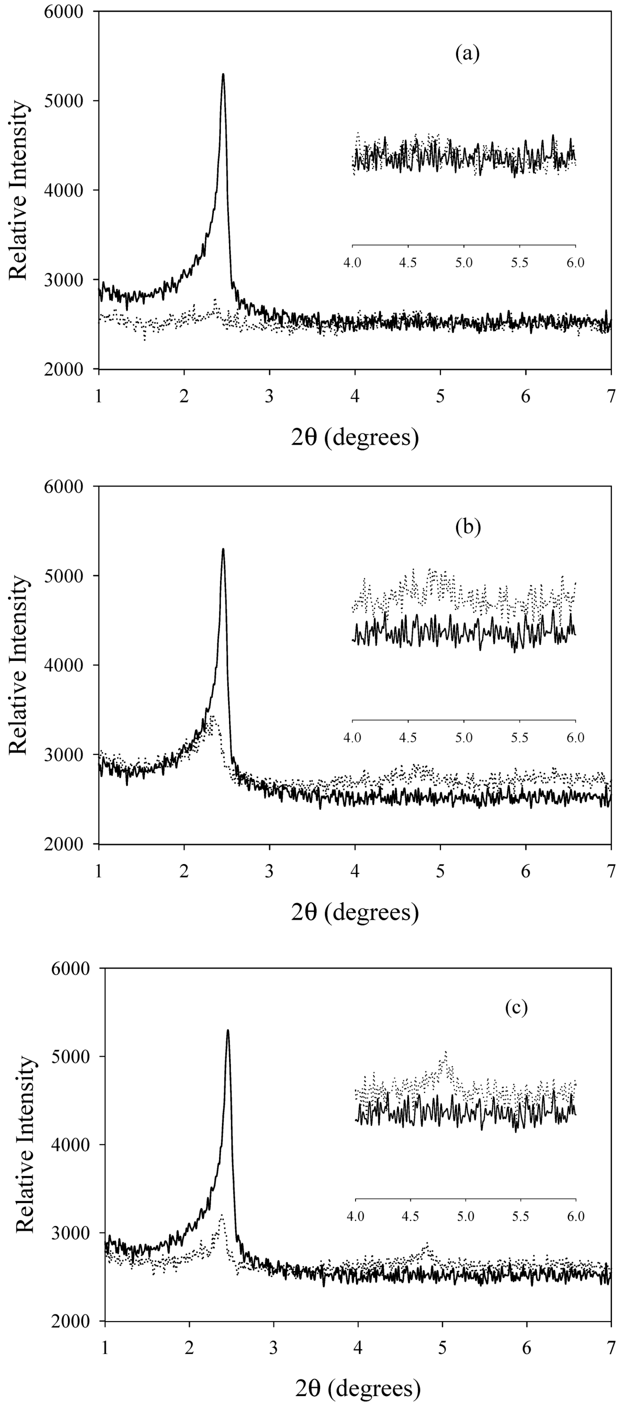

Figure 8. SAXS profiles for the hexagonal phase formed with 50% PM1−20% DTAB in water using (a) I-2959 at 1 mW/cm^2, (b) I-651 at 1 mW/cm^2, and (c) I-651 at 15 mW/cm^2 before (—) and after (···) polymerization.

surfactant the LLC order preservation after polymerization might also be influenced. Figure 8a shows the SAXS profiles for the hexagonal phase formed at 50% PM1/20% DTAB in water before and after polymerization using I-2959 and polymerized with a low light intensity of 1 mW/cm^2. As shown in Figure 3 the hexagonal phase formed by using PM1 exhibits significantly less order compared to C12MA. This behavior is confirmed by SAXS before polymerization which shows only one reflection with much lower intensity than for C12MA, even when twice the time is used for data collection, indicating a much more disordered LLC. After polymerization with I-2959 the primary reflection is no longer evident suggesting that all order is lost. This behavior suggests that the degree of order in the LLC phase before polymerization plays a role in the order of the resulting polymer. The order is lost after polymerization for PM1, which exhibits less ordered hexagonal phases than C12MA.[13] For C12MA, even though order was decreased when using I-2959, a much greater degree of order was preserved.

When using I-651 which induces a higher reaction in initiating the PM1 system, significantly greater degrees of order are preserved as shown in Figure 8b. After polymerization the intensity of the primary peak decreases suggesting some order is lost after polymerization. The extent of the decrease in order is much lower compared to the system where I-2959 is used. Also, a secondary peak is observed after polymerization, indicating an increase in LLC order. Apparently, the increase in polymerization rate enables some retention of order by decreasing phase separation during polymerization. Interestingly, the order is preserved to an even larger extent when using I-651 with a light intensity of 15 mW/cm^2 as seen in Figure 8c. Before polymerization only a weak scattering peak is observed. After polymerization the intensity of the primary peak decreases but a secondary reflection appears suggesting some LLC order is retained. Both reflections are more defined compared to those observed when I-2959 and I-651 are used at low light intensity. Therefore, for both C12MA and PM1, higher polymerization rates induced by more efficient initiators or higher light intensity are required in order to allow retention of LLC order after polymerization. These results support the fact that the polymerization kinetics can be used to help govern LLC order preservation after polymerization for reactive LLC systems.

Conclusions

In this work, LLC order, polymerization kinetics, and LLC order preservation during polymerization of reactive LLC systems with different location of the reactive groups is detailed. The polymerization kinetics are highly influenced by the location of the reactive group in the LLC. When the reactive group is located near the polar head (C12MA), the polymerization rate increases as the LLC order increases. On the other hand, when the reactive group is located in the aliphatic chain of the reactive surfactant (PM1), the polymerization rate decreases as the LLC order increases. This behavior is due to segregation effects as indicated by determination of propagation and termination rates constants. The higher polymerization rates that reactive LLC systems exhibit with higher efficiency initiators improves the preservation of LLC order. The use of high light intensity for photoinitiation also aids in the LLC order preservation after polymerization. These results demonstrate that polymerization kinetics can be used to optimize order retention for reactive LLC systems.

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